Comparison of direct and Fourier space techniques in time-dependent density functional theory

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Abstract

Several techniques have appeared in the literature to solve the equations of time-dependent density functional theory. We compare the efficiency of different methods based on mesh representations of the wave functions (direct and Fourier space), taking as a test case the calculation of the surface plasmon in the cluster Na$_8$. For smaller systems, the methods have comparable efficiency. For large systems the direct time method has a decided advantage in computer storage requirements. It is also more economical on arithmetic operations, but is not as suited for parallel computing as the methods based on a frequency representation.

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I. INTRODUCTION

The time-dependent local density approximation has proven to be a useful tool to calculate the optical properties of finite systems such as atoms, molecules, and atomic clusters [1–8]. The basic equation to be solved is conceptually very simple, little more than the time-dependent Schrödinger equation for a particle in a time-varying external field. Many numerical methods are in use to solve the equations. On the one side there are quantum chemistry methods based on atomic orbital representation for the wave function, and on another side there are methods based on mesh representations. We only consider the latter here, but even in this category there are a number of published techniques. Most fundamentally, the time evolution can be calculated directly or in Fourier space, i.e. in terms of frequencies. The former method is practically a necessity for dealing with very strong external fields [10,11] and has been applied by two of us (K.Y. and G.B.) for the weak-field response as well [4]. We shall call this approach the "nuclear physics"(NP) method, since the algorithms were originally developed in that field for describing nuclear reactions [12]. The other methods we will consider [3,8] solve equations in frequency space. The method described in ref. [3] had its origins in condensed matter theory and uses Fourier representation for both space and time; we shall call this the "condensed matter" (CMP) method. We also comment on ref. [8] which uses Fourier space for the time but a real space mesh for the spatial dependence [13]. Here the problem is cast into a matrix diagonalization in the particle-hole representation; we shall call it the diagonalization method.

In this work we will compare the CMP code and the NP code for a specific system and present arguments for the scaling properties of the respective algorithms for larger systems. The system we choose to study is the atomic cluster Na_8, and in particular the surface

plasmon excitation which is seen as a strong peak at 2.5 eV excitation. The TDLDA is not an exact theory and it predicts a excitation energy at about 2.7 eV. We shall demand of both methods that they achieve within 0.1 eV of the converged value. It makes little sense to calculate to higher precision in view of the intrinsic limitations of the theory.

We shall now describe the various methods from a computational point of view. We shall use the symbol N with subscripts for quantities that scale roughly as the size of the physical system under study, and M for quantities that may be large but are independent of the size of the system. Important quantities common to the two codes are the number of electrons N_e and the number of mesh points, N_G and N_R for real space and reciprocal space, respectively. Additional quantities that play a role are the number of frequencies to be calculated M_ω, and the number of time steps to evolute the wave function in the real-time method, M_T. Also, in methods that rely on sparse matrix multiplication, we need the number of nonzero entries in a row of the Hamiltonian, M_H, and in iterative methods to solve large matrix equations we need the number of iterations for convergence, M_{it}. Finally, the response function method usually requires a sum over unoccupied states, N_c. This notation is summarized in Table I.

We will use same energy functional for all methods, so the choice of specific functional is not an issue in comparing the methods. As is commonly done, we calculate only the dynamics of the valence electrons. The core electrons are frozen and their presence is treated by using a pseudopotential to describe the ionic potential. We use the pseudopotential construction of Troullier and Martins [15], taking the nonlocal part by the method of Kleinman and Bylander [16] and including partial core corrections for the exchange-correlation energy [17]. In this method, the local pseudopotential is fixed to the value in a particular angular momentum channel, and a nonlocal correction is made for other channels. Here we use the $l = 1$ potential as the local potential, and apply the nonlocal correction to the $l = 0$ and $l = 2$ channels. The electron-electron interaction is taken in the simple local-density approximation (LDA) given by Perdew and Zunger [18]. More complicated functionals have better predictive power for ground state properties [6,7], but give only small improvement to the optical response of neutral molecules. The proper description of the 1/r asymptotic

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behavior of the potential is going to be very important to describe charged systems, however for the aim of the present work this LDA deficiency is not relevant.

The geometry of the Na$_8$ cluster was computed in ref. [6], and the lowest energy structure found to be the bicapped octahedron (D$_{2d}$ symmetry). We use this structure in our comparison here. It has an average Na-Na bond length of 3.38 Å and a slight deviation from the spherical symmetry. This leads to a polarizability tensor with two different components and two close-lying peaks are obtained in the photoabsorption cross section.

II. THEORETICAL METHODS

Before describing in detail each of the two methods for representing the wave functions (direct and Fourier space), we need to comment on the choice of the spatial cell size and mesh size as well as the time/frequency parameters (all are summarized in Table I).

Since the wave functions are sensitive to boundaries, the calculations must be made in a volume several Angstroms larger than the size of the molecule or cluster. Using both methods, we determined how large a volume is needed to achieved 0.1 eV accuracy on the various excitation energies of interest in the system. We found that this is achieved in a spherical volume of radius $R = 8$ Å using the NP code, and in a simple cubic supercell of side 12.7 Å using the CMP code. These have nearly the same volume, and thus the same average distance from the cluster to the boundary. We have checked the convergence of the results by increasing the volume to a sphere of 12 Å radius. The value of the plasma frequency is reduced by a maximum of 0.1 eV, that is, within the required accuracy.

We have used an uniform spatial grid with $\Delta x = 0.5$ Å spacing. This corresponds to a plane-wave cutoff energy of 6 Hartrees in the Fourier space method (see below). Within this parameters, a stable time-step to perform the time-evolution in the NP method is $\Delta t = 0.003\hbar/eV << \hbar(\Delta x)^2/m$. The required 0.1eV accuracy in energy is obtained for total simulation times of 10 $\hbar$/eV. Similarly in the Fourier space method we have taken a uniform frequency grid of $M_\omega = 100$ between 0 and 5 eV. Note that if the response is required for

larger frequencies we need to increase the number of points. The whole response is obtained at once in the time evolution method (unless up to energies of the order of $(\Delta t)^{-1}$). This is a great advantage when the whole response is needed.

A. NP method

This method uses a direct solution of the time-dependent single-electron Schrödinger equation,

$$i\hbar\frac{\partial\phi_i(\mathbf{r},t)}{\partial t} = H_{KS}(t)\phi_i(\mathbf{r},t) \quad (\text{i} = 1\ldots\text{occ.}) \tag{1}$$

where H_{KS} is the Kohn-Sham Hamiltonian operator

$$H_{KS}(t) = -\frac{\hbar^2}{2m}\nabla^2 + V_{ion}(\mathbf{r}) + e^2\int d^3r'\frac{n(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|} + V_{xc}(\mathbf{r},t) \tag{2}$$

and n is the time-dependent electron density $n(\mathbf{r},t) = \sum_{i=1}^{occ}\phi_i^*(\mathbf{r},t)\phi_i(\mathbf{r},t)$. In the solution of this equation in the spatial and time variables following the algorithm of ref. [4], there are two time-consuming operations. One is multiplying the single-electron Hamiltonian operator by the vector representing the wave function. The dimensionality of the vector is the number of mesh points N_R times the numbers of electron orbitals N_e. The operator is a sparse matrix with M_H nonzero elements per row. Thus the basic operation requires about $N_e N_R M_H$ complex floating point operations. The time evolution operator in the NP code is implements by a power series expansion of the exponential operator $\exp(-iH\Delta t)$ to fourth order. A predictor-corrector cycle requires two such operations. Thus the method requires 8 Hamiltonian multiplications per time step. Thus for M_T time steps the total number of floating point operations is given by

$$NPFPO : 10N_e N_R M_H M_T$$

The sparseness of the Hamiltonian matrix in a real space formulation is determined by the finite difference formula for kinetic energy (nine-point formula in our case); and by the

nonlocal-projection parts of the potential. In total we have a number of non-zero elements of the each Hamiltonian row $M_H \approx 100$ for the grid parameters used for Na$_8$.

The other time-consuming part of the NP algorithm is solving the Poisson equation, which must be done twice at each time step. The NP code uses a multipole expansion combined with a relaxation method to deal with the higher multipoles. It is hard to estimate the scaling properties of this part, but in the present study this part of the computation takes 1.5 times as many operations as the Hamiltonian multiplication operation. We shall assume the same factor for estimating the scaling properties of the algorithm. In principle, the Poisson equation can be solved by methods that are of order N_R or $N_R \log N_R$, as multigrid or fast-Fourier transformation, so this part should not dominate for large system.

Storage requirements are small: the vector wave function plus $V_{Hartree}$ and V_{ion} local potentials in Hamiltonian, charge densities and some intermediate arrays. $V_{Hartree}$ requires a slightly larger volume because of the way the Poisson equation is solved.

$$\text{NP storage}: \quad N_R(N_e + 4.5)$$

This NP method is ideal to be combined with molecular dynamics simulations for the ions because it uses only ground-state occupied information and would scale roughly linearly with the number of atoms in the system. There is not so much book-keeping as in the usual perturbative formalism (no need for storing the large set of unoccupied wave-functions and the large dielectric matrices).

B. CMP method

Here the basic object of the calculation is the linear response to an external field of some frequency ω. The linear response matrix χ is constructed in momentum space with the following matrix inversion

$$\chi = (1 - \chi_0 K)^{-1} \chi_0 \tag{3}$$

where the independent particle response χ_0 and the interaction K are matrices defined as follows. The χ_0 has elements G, G' given by [19]

$$\chi_0(\mathbf{G}, \mathbf{G}', \omega) = \frac{1}{\Omega} \sum_{kj} (f_k - f_j) \frac{\langle k|e^{-i\mathbf{G}\cdot\mathbf{r}}|i\rangle \langle i|e^{i\mathbf{G}'\cdot\mathbf{r}}|k\rangle}{\omega - \epsilon_j + \epsilon_i + i\eta} \tag{4}$$

where Ω denotes the unit-cell volume, i, k label Kohn-Sham eigenfunctions and ϵ_k and f_k are the corresponding eigenenergies and occupancy factors. The sum goes over N_e occupied orbitals and N_c empty orbitals. The interaction K is the Fourier transform of the electron-electron interaction in the Kohn-Sham equation, which is given in coordinate space by

$$K(\mathbf{r}, \mathbf{r}') = \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta V_{xc}(\mathbf{r})}{\delta n(\mathbf{r}')} \tag{5}$$

We now describe the computation starting with the Kohn-Sham wave functions and energies in a momentum space representation. To evaluate the independent particle response χ_0 in eq.(4), one first calculates the particle-hole matrix elements of the momentum operator and stores them in a table (or in disk). This computational effort is of the order of $N_e N_c N_G^2$ operations, and the table size to be stored is $N_e N_c N_G$ complex numbers. Then the evaluation of eq. (4) requires N_G^2 matrix elements to be calculated, each requiring particle-hole summation, to give $\approx 2N_G^2 N_e N_c$ operations for each frequency. If one were to make full space calculation, the number of empty orbitals summed in eq. (4) would be of the same order as the dimensionality of the space. However, the number of empty orbitals can be severely truncated without effecting the long-wavelength dipole response. In the example, we find $N_c = 320$ is adequate, which is more than an order of magnitude smaller than the size of the space and corresponds to include unoccupied states up to 20 eV above the highest-occupied orbital. This is a reasonable approximation as we are interested only in getting the optical spectra for excitation energies below 10 eV. This approximation is an important saving in building up the response matrix.

One also truncates the calculation of the response matrix in another way. We have also assumed that the off-diagonal elements of the response function are zero for G-vectors outside an sphere of 1.25 Å (that is to consider ≈ 3200 points in the G-space). This corresponds to

reducing the number of matrix elements to be computed and stored to $N_G(N_G+4)/18$. Note that the necessity to store the N_G^2 matrix puts a higher demand on the computer memory than the NP method. The memory required to store the N_G^2 complex, double-precision numbers in the example problem is 164Mb.

There are now three steps to evaluate eq. (3), two matrix multiplications and a matrix inversion. The matrices are not sparse, so the matrix multiplications each cost $2(N_G/3)^3$ arithmetical operations [1]. The matrix inversion is of the same order, requiring $(N_G/3)^3$ operations. The total is $\approx 5(N_G/3)^3$. These represent the most computationally demanding steps in the CMP method, given the truncation in the N_c. The computed χ is next transformed to the coordinate space representation. Using the fast Fourier transform, this takes $\approx N_G^2 \log N_G$ operations. The dynamical polarizability can be now computed from $\alpha(\omega) = V_{ext}\chi V_{ext}$ as a matrix times vector multiplication. From this one can easily extract the photoabsorption cross section $\sigma(\omega) = \frac{4\pi\omega}{c} Im\alpha(\omega)$.

Then the total computational effort in the CM method is:

$$\text{CM FPO}: \quad M_\omega(N_c N_e (N_G/3)^2 + 5(N_G/3)^3)$$

with the last term dominant. The storage requirements for all the occupied and unoccupied wave functions plus the whole complex response matrix is

$$\text{CM storage}: \quad (N_e + N_c)N_G + 2(N_G + N_G^2/9) + N_c N_e N_G/3$$

To achieve the targeted energy convergence with this algorithm, the momentum space mesh was chosen to correspond to a simple cubic supercell of $L = 12.7$ Å on a side. This implies that the mesh spacing in momentum space is $\delta k = 2\pi/L = 0.137$ Å. The momentum space representation takes all the points within a sphere of radius $k_{max} = 1.83$ Å (that

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[1] A small technical point should be mentioned, associated with the divergence of the Coulomb interaction at $\mathbf{G} = \mathbf{G}'$. This is dealt with [19] by taking a numerical limit as $|\mathbf{G} - \mathbf{G}'| \rightarrow 0$, and this adds about 10% to the number of operations for computing the matrix product.

corresponds to a plane-wave cutoff energy of 12 Ry). The size of the vector in the momentum representation is thus $N_G = 4\pi(k_{max}/\Delta k)^3/3 \approx 10,000$. Note that this is slightly smaller than the number required for the coordinate space representation, however we need to stress that a larger number of G-vectors are needed to describe the action of the potential on a wave-function ($V\psi$ corresponds to a convolution in Fourier space). Finally, an additional numerical parameter is the imaginary part of the frequency η, which we have taken as $\eta = 0.05$ eV to produce a resolution of 0.1 eV in the spectral features.

In the discussion below we have not include the computational requirements to perform the ground state calculations, occupied and unoccupied orbitals. This could be a major storage bottle-neck for very large systems as the calculation of a large set of unoccupied wave functions has a cubic scaling of the number of atoms in memory and computing time. In the present calculation this initialization process takes 10% of the total computational time.

C. Other methods

We mention here two other methods from a computational point of view. Since we have not carried out numerically computations on our test problem with these methods, the discussion will be brief.

1. Modified Sternheimer method

The modified Sternheimer method was first applied to the time-dependent Kohn-Sham equation for atomic excitations [20], and has since been applied to the dielectric response of crystals using the momentum space representation [21] and to the finite system C_{60} [22] using the coordinate space representation. Here one solves an inhomogeneous equation for the perturbed wave functions $\phi_i^{\pm}$ using an iterative method. The perturbation is a sinusoidal potential field combining the external field V_{ext} and the internal field from the time-varying electron density. The equations are

$$(\epsilon_I - H^0_{KS} \pm \omega + i\eta)\phi_i^{\pm} = \hat{P}V_i \tag{6}$$

where

$$V_i = (V_{ext} + K\delta n)\phi_i$$

and

$$\delta n = \mathrm{Re} \sum_i \phi_i(\phi_i^+ + \phi_i^-). \tag{7}$$

$\hat{P}$ is a projection operator removing occupied orbitals. In ref. [22], the two equations are constructed in coordinate space and solved with a double iteration. One makes a guess for the density δn, and solves eq. (6) by the conjugate gradient method. δn is refined from the resulting $\phi_i^{\pm}$ again with the conjugate gradient method, and the process is repeated to convergence. The numerical cost will thus depend largely on the cost of the Hamiltonian operation which is $\approx M_H N_R N_e$ in coordinate space, and the number of iterations M_{it} required to get a converged solution. Remembering also that frequency space methods need M_ω, the number of frequencies to be examined, the computational cost of this method is

$$\text{Modified Sternheimer (real space)}: \quad M_\omega M_{it} M_H N_R N_e \tag{8}$$

The method can be used in this form for nonresonant frequencies, but near the eigenfrequencies the nearby singularities in eq. (6) must be removed for the conjugate gradient method to converge. Thus this method would be similar to methods utilizing the particle-hole representation in needing a considerable number of the wave functions and eigenenergies of unoccupied states. The singularities are removed by projecting on the unoccupied wave function subspace the right hand side of eq. (6),

$$V_i' = V_i - \sum_j \phi_i(\phi_i, V_i).$$

The desired wave functions $\phi_i^{\pm}$ are obtained from the projected solutions $\phi_i'^{\pm}$ by

$$\phi_i^{\pm} = \phi_i'^{\pm} + \sum_j \frac{\phi_i(\phi_i, V_i)}{\epsilon_j - \epsilon_i - \omega - i\eta}.$$

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It is difficult to give an *a priori* estimate of M_{it} or its size-scaling properties (although with our notation we have assumed that it does not grow with N). Unfortunately, our implementation of eq. (7) still left the convergence somewhat erratic. Typically it takes of the order of $M_{it} \approx 1000$ iterations of the double loop to get convergence. Thus it would require some improvement of the algorithm to make it attractive to apply to large systems.

The momentum space implementation of the modified Sternheimer method is similar. This method also needs the conditioning step for convergence of the CG iteration. The main difference is in the Hamiltonian multiplication, which here requires $\approx 2(N_G/3)^3$ operations as discussed in Sect. IIB. Thus the total is

$$\text{Modified Sternheimer (momentum space)}: \ 2M_\omega M_{it}(N_G/3)^3 \tag{9}$$

Because the Hamiltonian operation is more costly in momentum space, this method is probably not competitive to the others, unless it were the case that the convergence of the iteration were intrinsically much more reliable.

2. Diagonalization method

The frequency-space methods discussed so far have relied in some way on operator inversion. It is also possible to cast the problem as one of matrix diagonalization. This method was applied to cluster excitations in the TDLDA by Vasiliev et al. [8]. The authors start from a basis in coordinate space and construct Kohn-Sham orbitals for both occupied and empty states as is done in the CMP method, but representing the orbitals in coordinate space mesh, as in the NP method. The storage requirement for the orbitals is $\approx (N_c + N_e)N_R$, which is larger than in the NP method but smaller than in the CMP method.

The next step of the calculation is to construct the matrix to be diagonalized. The eigenvalue equation to be solved is

$$\mathbf{R}\mathbf{F}_n = \omega_n^2 \mathbf{F}_n \tag{10}$$

where $\mathbf{F_n}$ are the eigenvectors and $\mathbf{R}$ is a matrix. Its elements are

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$$R_{\alpha,\alpha'} = (\epsilon_i - \epsilon_j)^2 \delta_{\alpha,\alpha'} + 2\sqrt{(\epsilon_i - \epsilon_j)(\epsilon_i' - \epsilon_j')} K_{\alpha,\alpha'} \tag{11}$$

where the indices $\alpha = (ij), \alpha = (i', j')$ label combinations of unoccupied orbitals i and occupied orbitals j. The interaction matrix elements $K_{\alpha,\alpha'}$ are simply the particle-hole matrix elements of the residual interaction, eq.(5). There is a substantial computational cost in construct the interaction matrix K. A straightforward transformation from the coordinate space to the particle-hole representation requires $\approx N_R^2 N_e^2 N_c^2$ operations for the Coulomb interaction. However, this is reduced considerably by using an efficient method to solve the Poisson equation [9]. For example, using the fast Fourier transform one may find the Coulomb field for a given particle-hole state taking only $N_R \log N_R$ operations. Saving the Coulomb field in the coordinate representation, the matrix element to a given final state takes $\sim N_R$ operations. The effort of solving the Poisson equation is thus distributed over the number of final states, and the operations to construct the full matrix has a leading dependence $N_R N_e^2 N_c^2$, the scaling appropriate for the local part of the interaction[2]. Once the matrix is constructed, the diagonalization requires $\approx (N_c N_e)^3$ operations. However, taking the N values from Table I, the matrix diagonalization effort is small compared to that needed to construct the matrix. We have therefore taken that step to assign this method's size scaling in Table II.

III. NUMERICAL RESULTS

We will discuss in detail the physical quantities computed in the NP and CMP methods and refer to [8] for the results using the diagonalization method. We want to stress that the three approaches must give the same values if the numerical parameters are chosen with fine enough grids and large enough cutoffs to get converged results.

With the parameter sets chosen for the two methods, the results are quite similar. In Table IV we show calculated Kohn-Sham energies and the surface plasmon energy. The

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[2]However, in the implementation of ref. [8], the Poisson solver in fact is the most costly operation.

first entry ϵ_1 is the Kohn-Sham eigenvalue of the most bound orbital. The absolute energies have no significance in the supercell method, because the absolute Coulomb potential is undefined. Therefore, for this entry we give the value from the NP code and set the scale of the CMP energies at that value. The next three rows correspond to the other bound orbitals use the $G = 0$ point of the Brillioun zone for the CMP values. We can see that the methods agree to within less than 0.1 eV. The next entry is the lowest unoccupied orbital. This is significantly different for the two methods. This orbital has sufficient extension to have its energy sensitive to the boundary, which of course is different for the two methods. We confirm the boundary sensitivity in the CMP code by calculating the energies at other points in the Brillouin zone. Differences are less than 0.1 eV for occupied orbitals, but reach 0.2 eV for the lowest unoccupied orbital. This last point indicates the fact that the empty orbitals are more sensitive to the boundary conditions and in the periodic supercell they feel the potential from the other clusters.

We have also presented in Table IV the results of the NP method [3]. We have also checked the convergence of the plasmon frequency with respect to the cell size and found that this value is converged to less than 0.01eV for a sphere of R=12 Å. The fully converged value in the NP method is 2.65 eV. The difference with the experimental value of 2.53 eV can be attributed to deficiencies in the LDA approximation as well as for finite temperature effects in the experiments [6].

In Table V we summarize the results for the static averaged electrical polarizability of Na$_8$ obtained by the different methods. The agreement among the different approaches is very good and the remaining difference with experiments can be again assigned to core

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[3]The plasmon frequency is sensitive to the core-exchange correction at the level of 0.1 eV. We have included that correction in H_{KS} it improves the description of the structural properties of Na metal. We note that the result without core corrections (2.89 eV) it is very close to the jellium value (2.9 eV).

polarization, exchange-correlation and temperature effects. These effects tends to increase the polarizability bringing the computed values close to the experiments [6].

IV. CONCLUSIONS

In the theory of electronic excitations of finite many-electron systems, the time-dependent Kohn-Sham equation with an adiabatic local density approximation for the interaction energy function offers an attractive compromise towards the goals of accuracy and computational practicality. But even within the TDLDA scheme there are several methods in use, and our purpose was to compare them on the same footing by applying them to the same physical problem, and demanding the same accuracy. The goal is to gain a general understanding of the numerical resources (total numbers of arithmetic operations and computer memory) required by the different methods. One can then extrapolate to large systems and make a judgment on which methods offer the best prospects.

We have only considered methods based on a grid representation of the electron wave functions, and have concentrated on two algorithms, the NP method in real time and real space, and the CMP method in Fourier transformed time and space.

We chose to study the response of the Na_8 cluster around the surface plasmon excitation energy. The two methods turned out to have comparable requirement on arithmetic operations. However, it should also be noted that the computational work increases with the range of frequencies that one studies in the CMP method, but not in the NP method. With latter, the entire response is obtained from a single calculation.

In comparing the two methods to ascertain their scaling with the size of the system N, we have deliberately ignored the first task in either method, the construction of the eigenstates of the static Kohn-Sham operator. In the NP method only the occupied orbitals are needed, but in the CMP method one also needs a large number of unoccupied orbitals as well. Their calculation scales like N_e^3 in principle, but in practice this phase of the computation is short compared to the dynamic calculation and so we ignore it. Let us now compare the scalings

by taking the expressions in Table II, dropping the subscripts on the N quantities. The NP method thus scales as N^2. This behavior was also found studying the excitations of long carbon molecules [5]. The CMP method has a poorer scaling behavior, namely N^3. We also considered two other methods without however examining them in as much detail. In principle, the modified Sternheimer method in coordinate space can achieve N^2 scaling without the cost of the large M_T factor of the real-time method. However, we did not find a reliably converging iteration procedure to solve the basic inhomogeneous linear equation set. The final method we discussed, the diagonalization method using real space and Fourier time, seems to have a poorer N-scaling than the others, but may be advantageous in some circumstances (see below).

Besides arithmetic operations, storage can play a role in the practicality of the different algorithms for large systems. Here we find that the storage requirements are grossly different for the NP and CMP methods, favoring the NP approach. From Table II, it has a N^2 scaling while the CMP method has an N^3 behavior. This is already significant in the Na_8 system we studied, as may be seen from Table III.

Thus our results favor the real-time and real-space methods, offering economy in both storage and arithmetic operations. However, there are a number of caveats. We have not considered the suitability of the different algorithms for parallel computing. In a parallel computing environment, the frequency-space methods gain favor because the M_ω factor can be trivially absorbed in the parallel processing. In addition, the diagonalization method can benefit from the parallel computation of different rows of the matrix. Also the sparseness of the Hamiltonian matrix is important for the real space method; this would be lost if for example the energy functional used the full Fock exchange interaction.

Finally, we mention two nonnumerical benefits of the real-time method: as was said earlier, it is nonperturbative and therefore allows effects of large fields to be calculated with the same effort. And it uses the same energy functional (permitting the program to call the same subroutine) for the dynamic calculation as for the static calculation to prepare the ground state.

V. ACKNOWLEDGMENT

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the other hand, the matrix elements in the response function cannot be calculated as easily as in a plane-wave reresentation and the check of convergence with respect to the size of the AO-basis set is rather difficult (usually the number of AO's is much less than N_G).

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TABLES

TABLE I. Symbol definitions for quantities pertaining to the computational effort required by the various algorithms discussed in the main text, and their values.

Symbol	Meaning	NP method	CMP method
M_T	time steps	10^4	-
M_ω	number of frequencies	-	10
M_H	nonzero elements in H matrix row	100	-
M_{it}	iterations in conjugate gradient method	-	-
N_R	real-space points	$17,000$	-
N_G	reciprocal-space points	-	9,771
N_e	number of electron orbitals (occupied states)	4	4
N_c	unoccupied states	-	320

TABLE II. Leading-order for the size scaling of various algorithms for TDLDA–general comparison: floating point operations (FPO) and memory requirements.

Method	FPO	Memory
NP	$N_e N_R M_H M_T$	$N_R(N_e + 4.5)$
CMP	$5M_\omega(N_G/3)^3$	$N_G^3/9$
Modified Sternheimer	$M_\omega M_{it} M_H N_e N_R$	$N_R(N_e + N_c)$
Diagonalization	$N_c^2 N_e^2 N_R$	$(N_c N_e)^2$

TABLE III. Comparison of computational difficulty of NP and CMP methods for Na_8

Resource	NP	CMP
Memory (MBy)	7	350
Floating point operations	1.5×10^{12}	1.7×10^{12}

TABLE IV. Orbital energies ϵ_i and surface plasmon energy ω_M in Na$_8$. For comparison in parenthesis we show the result of a calculation within the NP method without including partial core corrections in the pseudopotential generation and time evolution.

Energy	NP	CMP	Exp. (eV)
ϵ_1	-4.63	-4.63	
ϵ_2	-3.41	-3.35	
ϵ_3	-3.00	-2.97	
ϵ_4	3.00	-2.97	
$\epsilon_5(LUMO)$	-1.88	-2.01	
ω_M	2.77	2.6	2.53 [23]

TABLE V. Static polarizability of Na$_8$ ($\text{\AA}^3$)

Exp.	NP	Atomic	CMP	All-electron
128.7 [24]	103	117 [8]	119	114.9 [25]